OFFICE OF NAVAL RESEARCH

CONTRACT N00014-95-1-0028

R&T Code 33e 1806

Dr. Richard S. Miller

Technical Report No. 92

# COMPUTED HEATS OF FORMATION OF DIFLUORAMINE ANALOGUES OF RDX AND HMX

by

Peter Politzer, M. Edward Grice and Pat Lane

Department of Chemistry
University of New Orleans
New Orleans, LA 70148



June 18, 1996

# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188



| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | June 18, 1996 | Technical Report |

**4. TITLE AND SUBTITLE**
Computed Heats of Formation of Difluoramine Analogues of RDX and HMX

**5. FUNDING NUMBERS**
N00014-95-1-0028
Dr. Richard S. Miller
R&T Code 33e 1806

**6. AUTHOR(S)**
Peter Politzer, M. Edward Grice and Pat Lane

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**
University of New Orleans
Department of Chemistry
New Orleans, Louisiana 70148

**8. PERFORMING ORGANIZATION REPORT NUMBER**
92

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**
Office of Naval Research
Code 333
800 N. Quincy Street
Arlington, VA 22217

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

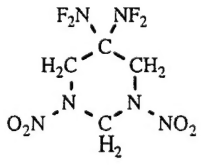
**11. SUPPLEMENTARY NOTES**

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**
Approved for public release.
Unlimited distribution.

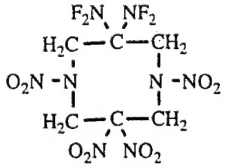
**12b. DISTRIBUTION CODE**

**13. ABSTRACT** *(Maximum 200 words)*

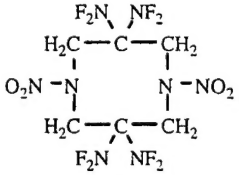
We have used our density functional procedure to compute the heats of formation of three difluoramine analogues of RDX and HMX, **1** - **3**.



**1**



**2**



**3**

Results:

**1**: $\Delta H_f^{298K}$ (gas) = 11 kcal/mole = 38 cal/g $\Delta H_f^{298K}$ (solid) = −21 kcal/mole = −75 cal/g

**2**: $\Delta H_f^{298K}$ (gas) = 5 kcal/mole = 13 cal/g $\Delta H_f^{298K}$ (solid) = −39 kcal/mole = −99 cal/g

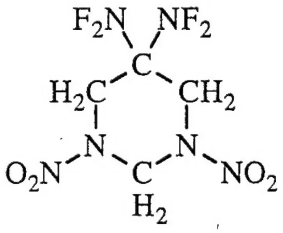
**3**: $\Delta H_f^{298K}$ (gas) = −24 kcal/mole = −58 cal/g $\Delta H_f^{298K}$ (solid) = −67 kcal/mole = −165 cal/g

For comparison, the experimental gas phase $\Delta H_f^{298K}$ value for RDX is 206 cal/g.

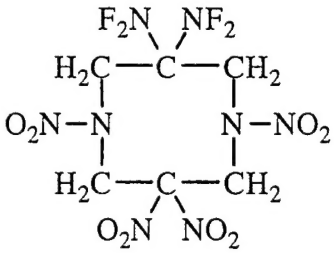
| 14. SUBJECT TERMS | 15. NUMBER OF PAGES |
|---|---|
| difluoramine analogues of RDX and HMX, heats of formation | 4 |
| | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| Unclassified | Unclassified | Unclassified | Unlimited |

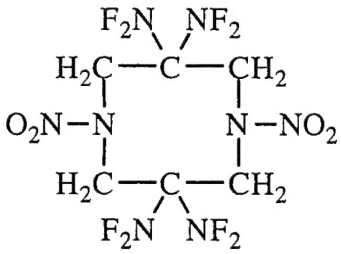
We have used our density functional procedure [1] to compute the heats of formation of three difluoramine analogues of RDX and HMX, **1** - **3**. The vibrational energies were determined from the molecular stoichiometries [2].



**1**



**2**



**3**

The density functional calculations give the gas phase heat of formation, which we convert to the solid state value by subtracting the heat of sublimation. We obtain the latter by means of the relationship that we have developed between the heat of sublimation and the computed electrostatic potential on the molecular surface [3].

The heat of formation of **3** was calculated for four different molecular geometries. Three of these were DF/BP86/6-31G** re-optimizations of HF/6-31G* structures sent by H. L. Ammon, University of Maryland, who imposed $C_i$, $C_2$ and no symmetry, to correspond to three polymorphs of **3**. We maintained the same constraints in the re-optimizations. The fourth geometry was computed directly at the DF/BP86/6-31G** level, with no imposed symmetry. Since the heats of formation obtained for these four structures covered a range of less than 4 kcal/mole, we will report only the results corresponding to the one with lowest energy; this is the density functional re-optimization of the HF/6-31G* geometry with no symmetry imposed.

Results:

**1**:

$$\Delta H_f^{298K}(\text{gas}) = 11 \text{ kcal/mole} = 38 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{solid}) = -21 \text{ kcal/mole} = -75 \text{ cal/g}$$

**2**:

$$\Delta H_f^{298K}(\text{gas}) = 5 \text{ kcal/mole} = 13 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{solid}) = -39 \text{ kcal/mole} = -99 \text{ cal/g}$$

**3**:

$$\Delta H_f^{298K}(\text{gas}) = -24 \text{ kcal/mole} = -58 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{solid}) = -67 \text{ kcal/mole} = -165 \text{ cal/g}$$

For comparison, the experimental gas phase $\Delta H_f^{298K}$ value for RDX is 206 cal/g [4, 5].

References:


1. D. Habibollahzadeh, M. E. Grice, M. C. Concha, J. S. Murray and P. Politzer, J. Comp. Chem. **16**, 654 (1995).
2. M. E. Grice and P. Politzer, Chem. Phys. Lett. **244**, 295 (1995).
3. M. DeSalvo, E. Miller, J. S. Murray and P. Politzer, unpublished work.
4. D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
5. J. M. Rosen and C. Dickinson, J. Chem. Eng. Data **14**, 120 (1969).